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SECOND VIRIAL COEFFICIENT OF NON-POLAR GASES AT MODERATELY HIGH TEMPERATURES

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ABSTRACT. A modified form of the Lennard-Jones (12-6) potential has been suggested by assuming a spherical hard core inside each molecule. An approximate expression for the second virial coefficient has been derived. The experimental second virial data on Ar, N_2, CO_2 and CH_4 have been compared with the calculated values.

The theoretical interpretation of the various gaseous macroscopic properties viz. equilibrium and transport, depends rather significantly on the potential energy function describing the force field between the molecules. The Lennard-Jones (12-6) potential had proved to be the most popular on account of its simplicity in handling and its realistic nature. The fact that this potential does not directly involve any parameter which may depend upon the size or the shape of the molecule makes its validity doubtful to some extent. Further this potential is found to be softer than required and a hard repulsion has been suggested to improve upon it. Kihara (195) and Pitzer (1955) introduced the idea of a convex hard core inside each molecule and thus modified the $L-J$ (12-6) potential. They suceeded in getting better agreement between theoretical and experimental data particularly on virials and viscosity. We here intend to investigate the following form of Lennard-Jones potential which also makes up the aforesaid deficiencies of the $L-J$ (12-6) potential to a certain extent :

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \text{ for } r \geqslant a\sigma$$

and $$\phi(r) = \infty \text{ for } r \leqslant a\sigma. \tag{1}$$

Here $\phi(r)$ is the potential energy at an intermolecular separation r, ϵ is the depth at which the potential energy minimum occurs, σ is the value of r at which $\phi(r) = 0$, and '$a\sigma$' is the diameter of the spherical impenetrable hard core assumed in each molecule. It may be noted that we have assumed a direct proportionality between core diameter and collision diameter. A simplified expression for the second virial coefficient based on the above function, eq.(1), is derived and its potentiality is tested through calculations for the gases *Ar*, N_2, Co_2 and CH_4.

According to the statistical mechanics the expression (Hirschfelder *et al*, 1964) for second virial coefficient, $B(T)$, for central potentials is given by

$$B(T) = 2\pi N \int_{\sigma}^{\infty} [1-\exp(-\phi(r)\,|\,kT)]r^2dr, \qquad .. \quad (2)$$

where N is the Avogadro's number and k is the Boltzmann's constant. The physical picture embedded in the potential function given by relation (1) modifies the expression for $B(T)$ as

$$B(T) = 2\pi N[\int_{\sigma}^{\sigma} \{1-\exp(-\phi(r)\,|\,kT)\}r^2dr$$

$$+ \int_{\sigma}^{\infty} \{1-\exp(-\phi(r)\,|\,kT)\}r^2dr, \qquad .. \quad (3)$$

$$= 2\pi N(I_1+I_2). \qquad (4)$$

The integral I_2 can be analytically solved by expanding the exponentil terms, the final expression is

$$I_2 = -\frac{\sigma^3}{3}[2.667(\epsilon\,|\,kT)+0.6095(\epsilon\,|\,kT)^2+0.1478(\epsilon\,|\,kT)^3$$

$$+0.0384(\epsilon\,kT)^4+..] \qquad .. \quad (5)$$

or in terms of the reduced temperature T^* $(= kT/\epsilon)$

$$= -\frac{\sigma^3}{3}\left[\frac{2.667}{T^*}+\frac{0.6095}{T^{*2}}+\frac{0.1478}{T^{*3}}+\frac{0.0384}{T^{*4}}+..\right]. \qquad .. \quad (6)$$

If we consider the temperature range for which T^* is greater than unity the series can be terminated after the fourth term without introducing an appreciable error. The integral I_1 can be written as

$$I_1 = 2\pi N\left[\frac{\sigma^3}{3}(1-a^3)-\int_{a\sigma}^{\sigma}\exp\{-\phi(r)/kT\}r^2dr\right] \qquad (7)$$

The solution of the second term of the R.H.S. of eq. (7) is not very straightforward. It may be noted here that its contribution as compared to the contribution of the other terms is considerably small. As such we have calculated it by employing the following approximations :

(a) In the short-range region the contribution of the dispersion energy term to the total potential energy is negligible, so that

$$\int_{a\sigma}^{\sigma}\exp\{-\phi(r)\,|\,kT\}r^2dr = \int_{a\sigma}^{\sigma}\exp\left\{-\frac{4\epsilon}{kT}\left(\frac{\sigma}{r}\right)^{12}\right\}r^2dr \equiv I_3 \qquad .. \quad (8)$$

Let us now put $r = \sigma - x$ where x is the distance measured from the position at which $\phi(r) = 0$ so that

$$I_3 = \int_0^{\sigma(1-a)} \left[\exp\left\{ -\frac{4\epsilon}{kT} \left(\frac{\sigma}{\sigma - x} \right)^{12} \right\} \right] (\sigma - x)^2 dx. \quad .. \quad (9)$$

(b) It is obvious that unless we go to very high temperatures the values of x are bounded to be very very small as compared to σ or r. Under this approximation the integral I_3 reduces to the following simple form

$$I_3 = \sigma^2 \exp\left(-\frac{4\epsilon}{kT} \right) \int_0^{\sigma(1-a)} \left(1 - \frac{2x}{\sigma} \right) \exp\left(-\frac{48\epsilon}{kT} \frac{x}{\sigma} \right) dx. \quad .. \quad (10)$$

In writing eq. (10) we have neglected all terms containing x^2/σ^2 and other higher powers. The integration of (10) by parts yields to

$$I_3 = \sigma^3 \left(\frac{kT}{48\epsilon} \right) \exp\left(-\frac{4\epsilon}{kT} \right) \left[\exp\left\{ -\frac{48\epsilon}{kT}(1-a) \right\} \left(1 - 2a + \frac{2kT}{48\epsilon} \right) + \left(1 - \frac{2kT}{48\epsilon} \right) \right]$$

$$\simeq \sigma^3 \left(\frac{kT}{48\epsilon} \right) \exp\left(-\frac{4\epsilon}{kT} \right) \left[1 - \frac{2kT}{48\epsilon} \right]. \quad .. \quad (11)$$

The contribution of the term involving $\exp\left\{ -\frac{48\epsilon}{kT}(1-a) \right\}$ is negligible even for sufficiently large values of T or T^* so that it can also be omitted.

Combining eqs. (4), (6), (7) and (11) we have

$$B(T) = \frac{2}{3} \pi N \sigma^3 \left[1 - a^3 - \frac{T^*}{16} \left(1 - \frac{T^*}{24} \right) \exp\left(-\frac{4}{T^*} \right) - \frac{2.667}{T^*} - \frac{0.6095}{T^{*2}} - \frac{0.1478}{T^{*3}} - \frac{0.0384}{T^{*4}} \right]. \quad .. \quad (12)$$

The assumptions involved in the derivation of the above relation limit its applicability to temperatures for which $T^* > 1$.

CALCULATION OF B(T)

We have calculated the second virial coefficients for four representative gases viz. argon, nitrogen, carbon dioxide and methane. These gases have been chosen

to study the behaviour of the potential function corresponding to structureless spherical, linear and spherically symmetric polyatomic molecules. The calculations have been made according to eq. (12) which is based on the modified potential function and the results have been compared with the experimental data as well as with the theoretically predicted values according to the usual $L-J$ (12-6) potential. The potential parameters for the four gases on the (12-6) potential have been taken from MTGL (1964) (Ar, $\epsilon/k = 122°K$ and $\sigma = 3.40A$; N_2, $\epsilon/k = 95.9°K$ and $\sigma = 3.71A$; CO_2, $\epsilon/k = 205°K$ and $\sigma = 4.07A$; CH_4, $\epsilon/k = 148.2°K$ and $\sigma = 3.817A$).

The determination of $B(T)$ from eq. (12) requires the values of the two potential parameters, ϵ/k and σ. The best way would be to determine these parameters as well as the third parameter 'a' through the experimental data on some appropriate bulk property in conjunction with the theoretical relation developed on the basis of the potential given by eq.(1). We have, however, adopted a short cut by using the potential parameters already determined for the usual L-J (12-6) potential and adjusting the value of 'a' to fit the experimental data. We thus arrive at the value of 'a' as 0.48, constant for all the gases studied here. This approach is of course not very much reasonable and makes eq. (12) with the value of 'a' suggested above a semi-empirical one. However, we feel satisfied with this approach in view of the fact that the value of 'a' thus obtained is practically of the same order as used by Pitzer (1955) ($a = 0.334$) and those obtained by Bae and Reed (1966) in case of Morse potential (Ar, $a = 0.398$; CO_2, $a = 0.585$; CH_4, $a = 0.457$).

The above mentioned procedure for choosing the value of 'a' was primarily followed due to the reason that it is not directly possible either theoretically or empirically to determine the value 'a'. It is, however, possible to take up the values of core diameter as calculated by Kihara(1953). But it is observed that these values when used in eq (12) yield $B(T)$ values very much in disagreement with the experimental results. It may be pointed out here that a similar study using the Morse potential has been made by Bae and Reed (1966). They also observe that the core sizes for Ar and CO_2 given by Sherwood and Prausnitz (1964) according to the Kihara model are too small considering the structure of the molecules. Further the large value of 'a' which we have taken seems to be physically justified as according to the present model we will have a finite potential energy at $r = a\sigma$. Hence to have the same repulsion contribution to $B(T)$ as given by Kihara (1953) potential values of 'a' must be correspondingly larger. By choosing a constant value for the reduced core diameter it becomes possible to have reasonably consistent values of true core diameters for the different molecules, directly varying as the collision diameters.

The $B(T)$ values calculated according to eq. (12) and those obtained on the basis of usual $L-J$ (12-6) potential, along with their deviations from the

Table 1

Comparison of the calculated and experimental B(T) values

Gas	Temp. °K	B(T) Exptl.	B(T) calculated			
			Eq. (12)	Deviation	L-J(12-6)	Deviation
Ar	142.6	−94.0	−95.80	+1.80	−95.69	+1.69
		−94.42		+1.38		+1.27
	173.2	−63.82	−66.83	+3.01	−66.44	+2.62
		−65.21		+1.62		+1.23
	223.2	−36.79	−39.02	+2.23	−38.77	+1.98
		−37.43		+1.59		+1.34
	273.2	−22.10	−22.71	+0.60	−22.56	+0.46
		−21.45		+1.26		+1.11
	298.2	−16.06	−16.91	+0.85	−17.05	0.99
		−15.76		+1.15		+1.29
	323.2	−11.17	−12.10	+0.93	−12.15	+0.98
		−11.24		+0.86		+0.91
	348.2	− 7.37	− 8.23	+0.86	− 8.06	+0.69
		− 7.25		+0.98		+0.81
	373.2	− 4.14	− 4.90	+0.76	− 4.71	+0.57
		− 4.00		+0.90		+0.71
	447.2	+ 3.72	+ 2.38	+1.34	+ 2.68	+1.04
	473.2	+ 4.99	+ 4.31	+0.68	+ 4.66	+0.33
	573.2	+10.77	+ 9.52	+1.25	+10.51	+0.26
	673.2	+15.74	+12.64	+ 3.1	+14.18	+1.56
	773.2	+17.76	+14.77	+2.99	+17.06	+0.70
	873.2	+19.48	+16.11	+3.37	+18.94	+0.54
N_2	277.6	− 8.5	− 9.73	+1.23	− 9.66	+1.16
	298.2	− 4.84	− 5.05	+0.21	− 5.31	+0.47
	310.9	− 2.0	− 3.03	+1.03	− 2.80	+0.80
	323.2	− 0.52	− 0.90	+0.38	− 0.77	+0.25
	348.2	+ 3.31	+ 2.64	+0.67	+ 2.96	+0.35
	373.2	+ 6.19	+ 5.69	+0.50	+ 6.20	−0.01
	398.2	+ 9.05	+ 8.23	+0.72	+ 8.89	+0.16
	427.6	+11.6	+ 9.41	+2.19	+11.72	−0.12
	444.3	+13.1	+11.90	+1.2	+13.14	−0.04
	460.9	+14.2	+13.01	+1.19	+14.30	−0.28

Table 1 (*Contd.*)

Gas	Temp. °K	B(T) Exptl.	B(T) calculated			
			Eq. (12)	Deviation	L-J(12-6)	Deviation
N_2	477.6	+15. 4	+ 14. 0	+ 1.40	+ 15.59	− 0.55
	510.9	+17. 4	+ 15.71	+ 1.69	+ 17.39	+ 0.01
	573.0	+20.36	+ 18.18	+ 2.18	+ 21.24	− 0.88
	673.0	+23 46	+ 20.69	+ 2.77	+ 24.21	− 0.75
CO_2	273.2	−145	−129.4	−15.60	−128.76	−16.24
	298.2	−124.6	−109.36	−15.24	−108.43	−16.17
	310.9	−112.7	−100.62	−12.08	− 99.93	−12.77
	323.2	−103.0	− 92.92	−10.08	− 92.28	−10.78
	344.3	− 88.8	− 81.14	− 6.66	− 80.71	− 8.19
	379.6	− 70.7	− 65.83	− 4.87	− 65.49	− 5.21
	398.2	− 61.2	− 57.80	− 3.40	− 57.41	− 3.79
	410.9	− 56.5	− 53.32	− 3.18	− 53.15	− 3.35
	444.3	− 44.6	− 42.96	− 1.64	− 43.12	− 1.48
	477.6	− 34.9	− 34.27	− 0.63	− 34.02	− 0.88
	410.9	− 26.4	− 26.92	+ 0.52	− 26.96	+ 0.54
	573.2	− 13.58	− 15.84	+ 2.26	− 15.73	+ 2.15
	673.2	− 1.58	− 2.97	+ 1.39	− 2.80	+ 1.22
	773.2	+ 6.05	+ 5.78	− 0.27	+ 5.64	− 0.41
	873.2	+ 12.11	+ 12.08	+ 0.03	+ 13.18	− 1.07
CH_4	273.2	− 54.1	− 53.49	− 0.61	− 54.02	− 0.01
	303.2	− 41.6	− 41.66	− 0.06	− 41.60	0.0
	323.2	− 34.3	− 34.78	+ 0.48	− 34.73	+ 0.43
	343.2	− 29.1	− 28.84	+ 0.26	− 28.76	− 0.34
	363.2	− 24.2	− 23.66	− 0.54	− 23.68	− 0.52
	383.2	− 19.5	− 19.12	− 0.38	− 19.29	− 0.21
	403.2	− 15.4	− 15.11	− 0.29	− 15.08	− 0.32
	444.3	− 8.1	− 8.21	+ 0.11	− 8.07	− 0.03
	477.6	− 3.6	− 3.64	+ 0.04	− 3.51	− 0.09
	510.9	0.0	+ 0.19	− 0.19	+ 5.61	− 5.61

corresponding experimental value, [Ar—Michels *et al* (1949, 1958), Whalley *et al* (1955); N_2—Gunn (1958); CO_2—Gunn (1958) and Mc Cormack *et al* (1951); CH_4—Gunn (1958) and Hamann *et al* (1955)] are recorded in table 1 as a function of temperature. It is clear from the listings of this table that the values calculated from eq. (12) are in reasonable agreement with the experimental values. The average absolute deviation of the two sets of calculated values from the experimental ones are 1.52 and 1.05 for Ar, 1.24 and 0.42 for N_2, 5.19 and 5.62 for CO_2, and 0.29 and 0.75 for CH_4, respectively. The values calculated according to the modified potential thus show better agreement than those calculated according to the L—J (12-6) potential in case of CO_2 and CH_4 while are a bit inferior in case of Ar and N_2. Thus a definite conclusion about the superiority of any of these potentials cannot be arrived at the moment. With properly determined potential parameters the results obtained through the proposed potential are definitely expected to be better than those given by the conventional $L-J$ (12-6) potential.

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